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Hygienic assessment of phthalate migration from plastic containers for drinking water

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Packaged drinking water is one of the optimal forms of providing the population with drinking water; therefore, the achievement of guaranteed quality of this product is an urgent task. Chemical components such as phthalates in packaging can migrate into drinking water and have a negative impact on human health. The aim of our work was to assess the levels of migration of phthalates (DEHP, DiBP, DNBP) into aqueous model media at various temperature conditions (temperatures of 20 °C and 40 °C) for 30 days from PET bottles. We examined 7 samples of polymeric packaging material (unused PET bottles with a volume of 6 to 19 liters) intended for drinking water. The measurement procedure was performed using gas chromatography with mass spectrometric detection (GC-MS). The results of our research showed that packaging made of polyethylene terephthalate is a source of chemical contamination of bottled water, which is based on the processes of migration of polymer components. The highest level of migration was obtained for di (2-ethylhexyl) phthalate (DEHP). No statistically significant differences were found between the temperature of the model environment and the concentration of phthalates. The results obtained indicate the need to include di (2-ethylhexyl) phthalate in the list of monitored sanitary and hygienic safety indicators in the technical regulations on the safety of packaged drinking water, including natural mineral water with established maximum permissible concentrations.

Keywords: drinking water, packaged in containers, PET bottles, bottled water quality, phthalates (di (2-ethylhexyl) phthalate; di (n-butyl) phthalate; di (isobutyl) phthalate), migration of chemicals, bottled water.

Introduction

Water safety and quality are fundamental to human development and well-being. In the modern world, sources of drinking and domestic water supply are exposed to chemical and biological pollution, the intensity of which in some cases exceeds the technological capabilities of purification and the natural ability to self-purify.

Every year the list of toxicants, including those that have not been studied, that enter the sources of drinking and domestic water supply, increases significantly, which leads to problems with ensuring the chemical safety of water. For the reasons noted, risks to the health of the population are formed due to the consumption of water that does not meet the established quality requirements.

Bottled drinking water is the optimal form of providing the population with drinking water, physiologically adequate, allowing to replenish the deficiency of microelements. Unlike tap water, the chemical composition of bottled water is constant, controlled and can be changed according to a given recipe [1]. Polyethylene terephthalate (PET) is the most common type of plastic used to make drinking water bottles. PET can be obtained in various ways, but the most widespread is the method of transesterification of dimethyl terephthalate with ethylene glycol, followed by polycondensation of the resulting diglycol terephthalate [2].

In addition to the main components used in the production of containers from polyethylene terephthalate, additives such as plasticizers, catalysts, dyes, stabilizers and others are introduced at various stages of the technological process[1]. Phthalates are used as plasticizers or substances that increase the flexibility and plasticity of polymeric materials. The most commonly used phthalates are di (2-ethylhexyl) phthalate (DEHP), di (isobutyl) phthalate (DiBP), and di (n-butyl) phthalate (DNBP). Since phthalate molecules are not covalently bound to the polymer [3], and the vapor pressure is low, phthalates slowly migrate from plastics into drinking water [4].

The presence of phthalates in packaged drinking water only poses a minor health risk if the requirements for the production and storage of bottled water are met. However, various studies have shown that not only plastic PET bottles, but also waterworks and distribution networks can be sources of phthalates in bottled water [5–7].

Requirements for the safety of packaged drinking water are established by the technical regulations of the Eurasian Economic Union on the safety of packaged drinking water, including natural mineral water[2], unified sanitary and epidemiological and hygienic requirements for products (goods) subject to sanitary and epidemiological supervision (control)[3], as well as sanitary and epidemiological rules and regulations establishing hygienic requirements for the quality of water packaged in containers[4].

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[1] GOST 32686–2014 *Bottles from polyethylene terephthalate for food liquids*. General specifications, 2014; TR CU 005/2011 *Technical Regulations of the Customs Union "On the safety of packaging"*, 2011. (In Russian)

[2] TR EAEU 044/2017 *Technical Regulations of the Eurasian Economic Union "On the safety of packaged drinking water, including natural mineral water"*, 2017. (In Russian)

[3] *Uniform sanitary and epidemiological and hygienic requirements for the goods subject to sanitary and epidemiological supervision (control)*, approved by the Decision of the Customs Union Commission dated May 28, 2010. No. 299. (In Russian)

[4] SanPiN 2.1.4.1116–02 *Drinking water. Hygienic requirements for the quality of water packaged in containers*. Quality control. Sanepidemsluzhba, 2002, p. 40. (In Russian)

The technical regulations do not establish requirements for the content of DEHP, DiBP, DNBP in water and model media. However, in accordance with the uniform sanitary and epidemiological and hygienic requirements for the goods subject to sanitary and epidemiological supervision (control) and SanPiN 2.1.4.1116-02 on hygienic requirements for the quality of water packaged in containers, the permissible content of di (2-ethylhexyl) phthalate in drinking water packaged in containers, depending on the category, is 6 μg / l for the first category and 0.1 μg / l for the highest category. The WHO recommended limit for DEHP in drinking water is 8 μg / L[5].

The purpose of this study: assessment of the levels of migration of phthalates (DEHP, DiBP, DnBP) into aqueous model media at various temperature conditions for 30 days from PET bottles.

Material and methods

Seven samples of polymer packaging material intended for drinking water were selected as objects of research. All prototypes were represented by unused PET bottles with a volume of 6 to 19 liters. The measurement procedure and sanitary and hygienic studies of polymer (packaging) materials were carried out on the basis of the chemical analytical center "Arbitrage" FSUE "VNIIM named after D.I. Mendeleev" using gas chromatography with mass spectrometric detection (GC-MS).

According to the analytical report, during the study, the levels of migration of phthalates (DEHP, DiBP, DnBP) into the aqueous model medium (distilled water) were determined at temperatures of 20 °C and 40 °C for 30 days. For research, samples of PET containers were cut into working fragments 4 × 5 cm in size; thus, the exposed surface of each fragment was 40 cm^2. The study of migration into the aquatic model environment was carried out under the following conditions: the number of working fragments — 2 pcs. (total area — 80 cm^2), the volume of the model solution is 40 cm^3 (for 2 cm^2 of the sample, 1 cm^3 of the model solution), the exposure time is 30 days, the temperature is (20 ± 2 °C / 40 ± 2 °C). After the end of the exposure, internal standards were introduced into the model medium (a solution of isotopically labeled substances: DBP-D4 — for measuring DBP and DBP; and DEHP-D4 — for measuring DEHP). Analytes were extracted from the model medium by liquid-liquid extraction into hexane (the volume of the extractant was 5 cm^3). An aliquot was taken from the hexane extract and instrumental analysis was performed by GC-MS.

Statistical processing of the data obtained was carried out using the computer program IBM SPSS Statistics 22. When summarizing the quantitative values obtained in the course of the study, the methods of descriptive statistics were used. Data that are normally distributed are presented using the arithmetic mean (M) and standard deviation (SD). The median (Me) is used to describe data whose distribution is different from the normal one, and the lower (Q1) and upper (Q3) quartiles (25^{th} and 75^{th} percentiles) are used as scattering measures.

When distributing indicators in the sample populations, the Student's t-test (t) and the Mann — Whitney U-test (U) were used. As a criterion of statistical reliability, no less than 95% confidence interval ($p < 0.05$) was chosen.

[5] *Guidelines for drinking-water quality*. 4^{th} ed. Geneva: World Health Organization, 2017 License: CC BY-NC-SA 3.0 IGO.

Results

In the course of laboratory studies of polyethylene terephthalate container samples within 30 days, migration of the desired phthalates into model aqueous media was revealed. The concentration of DEHP in the model solutions is presented in the range from 8.55 to 71.0 μg / L, and the concentration of DiBP in the range from 2.6 to 19.15 μg / L. The content of DNBP in the model media was below the threshold for determining the method — less than 2.6 μg / L. Thus, the maximum level of migration into model media was obtained for di (2-ethylhexyl) phthalate, then di (isobutyl) phthalate and di- (n-butyl) phthalate.

When analyzing the data obtained, it was found that with an increase in the temperature of the model medium, the concentration of DEHP increases (at a temperature of 20 °C — 14.5 (13.0–18.0) μg / L, at a temperature of 40 °C — 19.0 (13, 0-24.5) μg / L), however, these differences are not statistically significant ($U = 17{,}000$; $p = 0.362$) (Table 1). Also, in the study of all container samples, it was revealed that an increased concentration of DiBP was noted at a temperature of 20 °C — 8.1 ± 5.75 μg / l, and at a temperature of 40 °C — 7.53 ± 3.94 μg / l. However, during the statistical processing of the results, it was found that these differences are not statistically significant $t = 0.220$; $p = 0.830$) (Table 2).

Table 1. **Migration of di (2-ethylhexyl) phthalate into an aqueous model medium at temperatures of 20 °C and 40 °C, μg / L**

Name	20 °C			40 °C		
	Min	*Max*	*Me (Q25–Q75)*	*Min*	*Max*	*Me (Q25–Q75)*
DEHP	8,55	71	14,5 (13,0–18,0)	13	54,5	19,0 (13,0–24,5)

Table 2. **Migration of di (isobutyl) phthalate into an aqueous model medium at 20 °C and 40 °C, μg / L**

Name	20 °C				40 °C			
	Min	*Max*	*M*	*SD*	*Min*	*Max*	*M*	*SD*
DiBP	2,6	19,15	8,1	5,75	3,5	15	7,53	3,94

The results of our study showed that packaging made of polyethylene terephthalate is a source of chemical contamination of bottled water, which is based on the processes of migration of polymer components.

The content of DEHP in model solutions is 1.1–8.8 times higher than the WHO-recommended limit for the content of di (2-ethylxyl) phthalate in drinking water and 1.4–11.8 times higher than the maximum permissible concentrations established by the Unified Sanitary-Epidemiological and Hygienic Requirements for the goods subject to sanitary and epidemiological supervision (control) and sanitary and epidemiological rules and regulations that establish hygienic requirements for the quality of water packaged in containers.

The study did not confirm the correlation between the migration of phthalates into the model environment and the temperature of solutions (20 °C and 40 °C) within 30 days.

The results of the migration of phthalates into drinking water obtained in the course of the study correlate with the data of foreign studies [8].

Conclusion

In the study of the migration of di (2-ethylhexyl) phthalate, di (isobutyl) phthalate and di- (n-butyl) phthalate from 7 samples of PET containers intended for drinking water into an aqueous model environment for 30 days at temperatures of 20 °C and 40 °C, the residual concentration of the desired phthalates was revealed. The highest level of migration was obtained for di (2-ethylhexyl) phthalate. Statistically significant differences between the temperature of the model medium and the concentration of DEHP and DiBP have not been established.

The results obtained indicate the need to include di (2-ethylhexyl) phthalate in the list of monitored sanitary and hygienic safety indicators in the technical regulations on the safety of packaged drinking water, including natural mineral water with established maximum permissible concentrations.

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